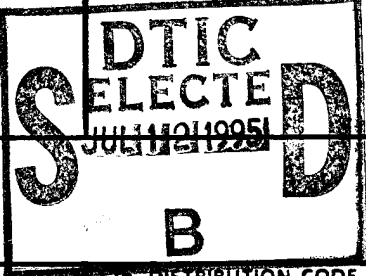


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High Resolution Electron Energy Loss Vibrational Spectroscopy:
Spectral Analysis and Information Depth**

by

Cara L. Weitzsacker, Joseph A. Gardella, Jr., Chantal Grégoire, and Jean-Jacques Pireaux

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Spectral Analysis and Information Depth**

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ABSTRACT

Langmuir Blodgett monolayers of a series of anthroyl substituted alkanoic (fatty) acid derivatives are used as model systems to study the interaction of low energy electrons with organic polymers in high resolution electron energy loss spectrometry. The variation of structure in the series effectively places the anthroyl functionality at various depths from the monolayer vacuum surface. The HREELS analysis of these systems provides a means to probe the depth dependence of vibrational energy losses. Maximum likelihood spectral restoration was used to establish more precise band energies resulting from energy loss, with comparison to infrared and Raman spectroscopic results for the compounds. These band energies were then used as initial values for curve fitting of the original data. The results of curve resolution aided in the estimation of the relative intensity of vibrational bands specific to the functional groups in the anthroyl sidechain and the aliphatic hydrocarbon backbone of the molecules in the films. By comparing vibrational intensities normalized to the elastic peak, it is shown that bands due to CH vibrations from saturated aliphatic structures are more surface sensitive than those due to aromatic structures. The comparison of the series of samples shows how the signals from aromatic structures decrease relative to aliphatic over a range of 15 Å from the vacuum surface.

INTRODUCTION

Low energy electrons (1 - 15 eV) impinging on a solid may excite electronic transitions or vibrational modes within chemical bonds near or at the surface. This interaction causes the electrons to lose energy in discrete amounts corresponding to the energy of the transition or excitation involved. This is the basis of high resolution electron energy loss spectrometry (HREELS) (1). As HREELS experiments have been applied to molecular and polymeric surfaces with increased chemical complexity (2-7), the *sampling* depth (the depth of excitation) and the *information* depth (the depth from which signals originate) have become important issues. Various empirical results have suggested the information depth may be as shallow as 2-5 Å to as deep as 20 Å (2,3-5).

The present study addresses the information depth of the HREELS experiment in more detail using a quantitative approach in a model system. In addition, full consideration of differences in vibrational excitation mechanisms and selection rules requires comparison to infrared and Raman scattering results. The following narrative summarizes current knowledge about mechanisms of vibrational HREELS and how they are experimentally distinguished for a particular band in a HREELS spectrum.

Vibrational Excitation Mechanisms in HREELS

The interactions between the primary electrons and the surface species leading to vibrational

energy losses can occur by three mechanisms: dipole scattering, impact scattering and negative ion resonance (8). These mechanisms determine the selection rules operating in the HREELS experiment. *Dipole scattering* is a long range interaction between the primary electron and the sample, on the order of 60 - 100 Å. This mechanism is dominant when the experiment is run in the specular geometry. This selection rule is the same as for infrared external reflection spectroscopies (6). When a dipole active mode is excited there is a change in dipole moment, and the vibrational mode is observed. In optical reflection spectroscopies with polarized radiation, when the dipole moment in a species is parallel to a metallic substrate, local electric fields are cancelled and vibrational excitation is not observed. Where the dipole moment is perpendicular to the substrate, the local electric fields are strengthened and the excitation is observed (1,6). This "surface selection rule", common for optical vibrational spectroscopies at metal interfaces, also applies to HREELS used to study adsorbates on a metal (1).

So called *impact scattering* is more prevalent when the experiment is run off specular or when higher energy primary electrons are used (1). This mechanism is short range, on the order of a few Å's. In this event, all vibrations in a molecule can be excited. The cross section for scattering changes with the geometry of the experiment (specular vs off specular) (1). The electrons inelastically scattered by this mechanism are broadly scattered such that fewer electrons are collected in the small acceptance angle of the analyzer. This diminishes the intensity of features due to impact scattering, as compared to the higher intensity of the dipole excited vibrations in the specular direction.

Resonance mechanisms were not reported in studies of small molecules adsorbed onto single crystal metals previous to 1982 (1,p.10). Resonance or negative ion resonance occurs when the primary electron energy corresponds to the energy of an unoccupied molecular orbital (MO) (e.g. the Lowest Unoccupied Molecular Orbital (LUMO)) of the adsorbed or surface molecules. This allows primary electrons to be temporarily trapped in the MO. The captured electron can remain in resonance for 10^{-14} to 10^{-12} seconds. The exit of the electron from the MO causes excitation of vibrations which enhances the loss features due to that vibration (1,7). Vibrational enhancement by resonance only occurs if the symmetry of the resonant state is compatible with the vibrational mode (9): the shape of the intermolecular bond which captures the electron is changed as the electron leaves. When this shape change corresponds to a vibrational mode, enhancement occurs. Vibrational modes which already result from dipole scattering may be enhanced by this mechanism. Changing the primary electron energy, so as to be in resonance with the unoccupied MO, will affect the loss features if they are enhanced by negative ion resonance.

While resonance enhancement of adsorbed molecules and thin films has been reported (5,7,10), many questions are still unanswered regarding this mechanism. When resonance will occur is not firmly understood. Resonance enhancement of vibrations from functional groups such as CH_3 and CH_2 has been observed in different materials (5,7,9,11). Whether the observation of enhancement of the same functionalities in several different compounds indicates that resonance enhancement can be predicted in similar cases is not known for certain. How resonance is affected by a material with many and various types of functional groups (for example: polymers or organic thin films) is a related concern. The extent or degree of enhancement for any given

functional group or material is also not well understood. Resonance enhancement in adsorbed films is an open research area with several groups working on the issues of concern (3,5,7-11).

If a firm understanding of the contributions of these mechanisms to band intensity can be developed with predictive capability, the sensitivity and selectivity of HREELS for *organic, or polymer thin film analysis* would be improved. For instance, the ability to selectively excite particular functional groups through resonance enhancement would allow less complication for identifying structures within a complex spectrum comprised of signals from functional groups of less interest (e.g. CH₃ and CH₂). This high sensitivity for the topmost surface may be exploited, for example, in the analysis of polymeric endgroup effects at surfaces (12).

Methodology

The model system used in this study was carefully constructed from set of three structural isomers (Figure 1). The sidechain anthroyl functional groups are oriented at different positions along a similar fatty acid methylene chain, at the topmost surface, at 12 Å and at 20 Å for 16AP, 12AS, and 2AP respectively.

HREEL spectra of organic films have low resolution and broad loss features. Unlike optical spectroscopies, in HREELS the instrumental contribution is broad and well known as the instrumental function can be defined by the measured elastic peak. Methods such as Fourier deconvolution (FD) or maximum likelihood restoration (MLR) (13,14) have been used to remove

the instrumental function and resolve the individual bands from the HREELS envelope (7,10,15-17). While MLR offers some specific advantages in for HREELS analysis because of the consideration of noise, and the ability to define the broadening function as related to the inherent elastic peak in the spectrum, it is not a simple solution to the problem (15,16). From experience in this research group (15), improvements in resolution are limited to reaching 30% of the original linewidth under ideal conditions.

Once a HREELS spectrum is better resolved and peak positions are better known, a curve fit can be applied for full interpretation. In the present paper, MLR is used to determine peak energies, in comparison to infrared and Raman results, and these are used within a peak fitting routine on the original data to determine band intensities. The goal of this approach is to quantify the changes in band intensity as the same functional group is at different distances from the surface in a similar material. Comparisons are made at two primary electron energies, 3 and 6 eV. Previous work (5, 7) has suggested resonance enhancement of aliphatic methylene functionality at the higher energy.

EXPERIMENTAL

Sample Preparation

Monolayers of 12-(9-anthroyloxy) stearic acid (12AS), 2-(9-anthroyloxy) palmitic acid (2AP), and 16-(9-anthroyloxy) palmitic acid (16AP) (Molecular Probes, Inc., Eugene, OR) (Figure 1)

were constructed using the Langmuir-Blodgett (L-B) technique. Each compound was dissolved in a hexane-ethanol solution (10:1 molar ratio) (18) to make up a solution of .5mg/ml concentration.

A KSV 2200 Langmuir trough (KSV Chemicals, Finland) was used to prepare the monolayers of the structural isomers. The Teflon trough has a 510 x 150 mm surface area. A Pt Wilhemy plate and surface balance is used to measure the film surface pressure. Film compaction and collection is controlled by electronics where the film barrier is slaved to the film balance. Both barrier speed and film pulling speeds are variable through set up in the electronics. The trough is located in a laminar flow hood mounted on a granite table.

A barium chloride / potassium bicarbonate subphase (3×10^{-5} M BaCl_2 , 4×10^{-4} M KHCO_3 in triply distilled water (19)) was utilized to form the carboxylate of the fatty acids, to lend stability to the film. The substrates used were Ge crystals which were cleaned by sonication in soapy water and then hexane and radio - frequency glow discharged previous to being set into the subphase. The solutions were cast onto the subphase by the slide method (20). The solvent was allowed to evaporate over 15 - 30 minutes. The barrier was then allowed to compress the film to a point of close packed as predicted from the isotherms of each molecule. The film was transferred onto a Ge crystal by Z-deposition and stored on a filter paper in a covered petri dish. The samples were then wrapped in kimwipes to prevent sliding and transported to Namur, Belgium for analysis by HREELS.

Instrumentation

The HREELS experiments were performed with a SEDRA High Resolution Electron Energy Loss Spectrometer (Riber I.S.A., France) (21). Two 180° hemispherical electrostatic condensers are used on the instrument. The electrons are extracted from a hot tungsten cathode with an electrostatic immersion lens and then go through the condenser to be monochromatized. The other condenser serves as the energy analyzer. The SEDRA is capable of an ultimate resolution of 5 meV for metals and approximately 3 meV for metal oxides. Elastic peak intensity is typically 10^4 counts/second (22). The instrument base pressure was approximately 7×10^{-11} torr.

All experiments were run in the specular 45°/45° geometry. Electron pass energies of 400 and 500 mV were used in the electrostatic condensers. Impact energies of both 3eV and 6eV were selected to investigate a possible resonance of the CH vibrational modes. Three eV impact energy is below resonance and 6eV is above resonance (5,7).

FTIR results were obtained by analyzing pellets of the pure compounds mixed with KBr. The analysis was done with a Mattson Sirius spectrometer using both 4 and 32 cm^{-1} resolution. 32 scans were collected for each sample.

FT-Raman results were obtained by the kind support of Dr. William P. McKenna of Kodak Research Laboratories. Data was collected by Dr. J. Guilment of Kodak-Pathe in France. A Bruker IFS-66 FT instrument, fitted with an FRA 106 FT-Raman attachment was used to collect

the data. The samples were irradiated using a Nd-YAG laser line at 1064 nm set at 100 mW power. 180° collection optics were used and the detector was a liquid nitrogen cooled Ge solid state device. 128 scans at 4 cm⁻¹ resolution were signal averaged for each spectrum. The neat compounds were loaded into melt capillaries for analysis. All three compounds were analyzed; the data from all compounds were similar in Raman scattering band energy and intensity.

Data from low resolution (32 cm⁻¹) FTIR and normal resolution FT-Raman are summarized in Table I.

Data Analysis

To better interpret the results of the HREELS of the three structural isomers, the software package Square Tools (Spectrum Square Associates, Ithaca, NY) was used. Two programs were utilized: Maximum Likelihood Spectral Restoration (or SSRES) and Curve Fitting (FIT).

From a quite large library of possible resolution enhancement routines, the maximum likelihood spectral restoration program (SSRES) was used for the opportunity offered to the user to define the instrumental peakshape- in our case, we synthesized a 'spectrometer function' by symmetrizing the shape of the left part from the elastic peak on the original spectrum- and the ability to consider experimental noise in the spectral calculation. The SSRES program (7, 10, 15-17) allows for input of the peak shape and width; this was taken as described above **from each specific spectrum to be analyzed**. Besides the original data, the operator must supply two

parameters; the broadening function (in our case the spectrometer function as defined by the symmetrized elastic peak) and an estimate of the noise level in the spectrum. The SSRES program provides a noise level estimate, in percent of the maximum signal. Typically, values estimated by the SSRES program were less than 1%. A more conservative value of 2-5 percent was chosen mainly because the program would estimate noise values from the elastic peak, and that is not a relevant estimate for the loss spectrum which is about 10 time lower absolute signal intensity in these spectra.

A natural concern in using this type of approach is the (ir)reproducibility of the output when used by different persons, because the peakshape synthesis could be variable from one to the other. Each data set was processed by SSRES several times by different operators. It was demonstrated within this laboratory that different users were able to achieve similar results, band energies were recovered within $\pm 20 \text{ cm}^{-1}$. The band energies of the recovered peaks also corresponded well to infrared or Raman active vibrations expected to be found in the HREELS spectra (**Table I**). This added confidence that the restoration could improve the resolution of the spectra while making physico-chemical sense.

For curve fitting the band positions recovered from SSRES analysis were used as the centroid values for the analysis of the original data. Again, the model peak function used for fitting was the symmetrized elastic peak, the same function used for the broadening function by SSRES. This yields a peak shape and FWHM. The FIT routine allows the initial estimation of peak position, shape, FWHM and intensity. The routine uses a procedure to minimize residuals and

allows the position and intensity to vary. The two main regions in the spectrum were fit separately; typically the CH stretch was fit by four to six bands and the rest of the spectrum from 1800 to -200 cm^{-1} , was fit using thirteen bands; the last three to simulate the elastic band. All initial peak positions were estimated with band energies from SSRES results. 50 to 100 iterations were allowed to reach convergence on a minimum χ^2 value.

RESULTS

Original HREELS Spectra

The original HREELS spectra (**Figure 2** and top traces on **Figure 3**) had a resolution (measured as Full Width at Half Maximum -FWHM- of the elastic peak) ranging from 145 - 200 cm^{-1} (16 - 25 meV). The spectra have broad features around 3400 - 2500 cm^{-1} (CH stretch region) and 2000 to 250 cm^{-1} ; they can be considered to consist of three components: aromatic, aliphatic and carbonyl/ester associated vibrational bands. The aliphatic bands include the CH stretch at 2920 cm^{-1} and the region including the 1440 and 1320 cm^{-1} bands (deformation modes). The aromatic bands include the CH stretch at 3060 cm^{-1} and the region including the series of bands at 1000, 890 and 750 cm^{-1} (aromatic ring deformation). The carbonyl/ester bands include the regions with the 1725, 1600 (C=O stretch) and 1170 cm^{-1} bands.

The analysis of results will follow four "regions" of interest (as defined in **Table I**) for each of the isomers and at each of the impact energies

16AP The comparison between 3eV and 6eV HREELS spectra for 16AP (**Figure 2a, b**) show the most differences due to impact energy. In the 3eV spectrum, the band in Region 1 which is centered at 3000 cm^{-1} (aromatic CH stretching) has a shoulder to the low energy side (aliphatic CH stretch). There is a distinct shoulder in Region 2 due to carbonyl vibrations. In Region 3, the peak centered at 1400 cm^{-1} (CH bending) is slightly resolved from a more intense peak at 1200 cm^{-1} (C-O ester stretching vibration). In Region 4, CH out-of-plane deformations appear as a peak centered at 900 cm^{-1} with a slight shoulder at 700 cm^{-1} .

The 6eV spectrum presents in Region 1 a flat top; the "aliphatic CH stretch" shoulder to low energy side has increased in intensity. The shoulder from the carbonyl (Region 2) is not as distinct as it was in the 3eV spectrum. The band in Region 3 is a broad peak centered at 1400 cm^{-1} as the aliphatic and ester vibrational modes are no longer distinguishable. The band in Region 4 is not as well resolved as in the 3eV and the shoulder feature at 900 cm^{-1} is not distinguishable.

12AS. The 3eV spectrum of 12AS (**Figure 2c**) also exhibits the CH stretching band centered at 3000 cm^{-1} . The crest of the peak corresponds to aliphatic CH stretching with a shoulder towards the higher energy side which corresponds to aromatic CH stretching. There is a slight shoulder in Region 2, corresponding to carbonyl stretching vibrations. Region 3 has a broad band centered at 1400 cm^{-1} (aliphatic CH bend) and a shoulder at 1200 cm^{-1} . Region 4 is a partially resolved band centered at 900 cm^{-1} . It is more intense than the corresponding peak in the 2AP spectrum (**Figure 2e**).

In the 6eV spectrum (**Figure 2d**), Region 1 is nearly the same as that of the 3 eV result. Within Region 2, the shoulder corresponding to carbonyl stretching is less distinguishable. The intensities of the CH bands (region 3) are reversed from that of the 3eV spectrum. There is no distinguishable shoulder at 1200 cm^{-1} . The intensity of the aromatic region (region 4) has not increased but is no longer resolved from the aliphatic region.

2AP. The spectrum collected at 3 eV (**Figure 2e**) has a peak centered at approximately 3000 cm^{-1} (Region 1) which is asymmetric towards the higher energy side. The peak position and shape indicate the presence of both aliphatic and aromatic CH stretches. The side of the peak above 3000 cm^{-1} is due to a lower intensity band of aromatic CH stretching. In Region 2, the bands near 1440 cm^{-1} are of higher intensity than the aromatic CH deformations in the region $1200 - 700\text{ cm}^{-1}$. The carbonyl region has no intensity of note. Region 4 is less intense than the aliphatic region but was partially resolved from the aliphatic region.

The 6eV spectrum has the same general character but with differences in intensities. Region 1 is slightly broader, with a shoulder to the higher energy side, indicating the presence of both aliphatic and aromatic CH stretches. The carbonyl region has no significant intensity. Region 3 is more intense than in the 3eV spectrum, while region 4 is no longer resolved from the aliphatic region but appears now as a shoulder. There was also an apparent intensity increase in region 4 with a shift of the broad feature to higher energies.

Maximum Likelihood Spectral Restoration

There are similarities between all of the Restoration results (**Figure 3**). For the CH region (3450 -2480 cm^{-1}), four to six peaks were found for all the HREELS spectra. For the 2000 cm^{-1} - down to the elastic peak region, 10 peaks were predicted for the majority of the spectra; in two cases, 11 peaks were predicted. All of the peaks were used to predict the band positions in the curve fitting using FIT (next section), but ten of these peaks were focused on for the examination of sampling depth: these ten peaks correspond to infrared and Raman active vibrations (**Table I**), i.e. those expected to be seen in the structural isomers.

The intensities of these recovered bands should reflect the IR absorptivity and the depth (relative to the topmost surface) of the functional groups found in the structural isomers. For each model compound, the band energy (i.e. peak positions) from different Restoration results obtained by varying the noise level parameter were compared and found to be reproducible within 3% relative standard deviation (RSD). This corresponds to $\pm 45 \text{ cm}^{-1}$ at 1500 cm^{-1} . The relative standard deviation of the peak positions for multiple runs ranged between .01 to 2.4 percent; one high RSD of 7.2 percent was obtained for the two SSRES results for 2AP 3eV. The IR and Raman active bands which are discussed below were consistently found in all of the SSRES results of the isomers.

The band energies from IR and Raman analysis of the neat compounds (**Table I**) were then compared to those calculated from the Restoration program. A typical comparison is shown in **Figure 4**. We found these peaks show up consistently throughout the restored spectra of the

three compounds, within 3 to 50 cm^{-1} of the infrared active band positions. These differences between the expected band position and that detected by the Restoration program are within reasonable experimental error. Indeed, due to the breadth and lack of resolution of the original HREELS spectra, some of the peaks had a larger difference than others. With an initial FWHM resolution of 145 - 200 cm^{-1} , a difference up to 50 cm^{-1} can be considered acceptable.

The comparison of the band intensities between the HREELS results from the monolayers of 16AP, 12AS, and 2AP is expected to provide a quantitative measure of the HREELS surface sensitivity, as the intensity of the peaks due to the carboxyl anthracene group should vary according to position. Since the intensity of the peaks could be distorted during the Restoration, the intensities will only be compared quantitatively from the curve fitting results from the original data. But it is already very clear that, qualitatively, the SSRES results do indicate differences in the structures of the three isomers (**Figure 2,3**).

First, the relative intensities of the CH stretching vibrations (3060 and 2920 cm^{-1}) are indicative of the position of the anthracene group on the long chain fatty acid: (1) for 16AP at 3 eV, the aromatic CH stretch (3060 cm^{-1}) is slightly more than two times more intense than the aliphatic CH one (2920 cm^{-1}); (2) the aromatic CH stretch is one third less intense than the aliphatic one in the 12AS spectra; (3) the aliphatic stretch is two and a half times more intense than the aromatic stretch in the 2AP spectra. These trends are the same in both the 3eV and 6eV spectra.

Second, the relative intensities of carbonyl associated bands (1750 - 1600 cm^{-1} region) show a

slight decrease in intensity in the comparison of the 16AP, 12AS and 2AP spectra (c.f. **Figure 2,3**).

Aliphatic associated bands ($1440 - 1300 \text{ cm}^{-1}$) are similar for the 2AP and 12AS spectra; the 1440 cm^{-1} band is more intense than the 1320 cm^{-1} one in the 3eV cases, but closer in intensity in the 6eV case. In the 16AP spectra, the 1440 and 1320 cm^{-1} bands are more intense in the 6eV spectra than at 3eV, this is at variance with the other two samples.

Curve Fitting Results

The band energies recovered from SSRES analysis (**Figures 3 and 4**) were used to set up the curve fitting (using the FIT program) of the original HREELS envelope. **Figures 5 and 6** illustrate these results for the 16AP and 2AP 3eV spectra. Comparing repeated calculations of the FIT program, the reproducibility of the band positions were within 1 to 25.5 cm^{-1} , with relative standard deviations from .01 to 2.10 percent, band by band. The differences between the infrared active bands and the FIT positions varied from band to band, in a range from 2 cm^{-1} to 65 cm^{-1} . Large differences are due to the band positions being allowed to vary during the FIT program. Again, due to the poor resolution of the original spectra, the deviation from the expected band positions is not unreasonable.

The results from curve fitting, compared to the SSRES ones, were judged to be reasonable from the correspondence of the band positions and relative intensities, as well as the goodness of fit as

expressed as χ^2 . All fits were allowed to continue until convergence or a minimum was reached. Two experimental HREELS runs of 16AP were collected at 3eV and 6eV. Two 12AS samples were run at 3eV and one at 6eV. One 2AP sample was run once for both impact energies. Minor differences were noted from run to run. All data was subjected to curve fitting results.

The SSRES band positions used to define the initial peak positions in FIT were consistent in all runs except the 2AP 6eV spectrum. There, the C=O stretch band was 90 cm^{-1} higher than the expected 1725 cm^{-1} band position (IR value); the IR active band position was used for the 2AP 6eV to maintain consistency between all the spectra. It was indeed expected that the intensity of the peak would be (very) low if the C=O was difficult to detect due to its "depth" in the film. Curve fitting was also attempted using the band energies from FTIR results; this gave a significant intensity at 1725 cm^{-1} . With the SSRES positions, the intensity at 1817 cm^{-1} was very low.

To analyze the intensity of bands as a function of the position of the anthroyl functional group with respect to the surface, the integrated areas of the bands recovered from curve fitting results were ratioed. The normalizing factor was the the integrated area of the elastic peak, as also recovered from curve fitting. This gives the normalized intensity of the peaks so the results between the three isomers can be compared. These values were split up into three sets: the C=O and C-O bands (1725,1600,1170 cm^{-1}), the aromatic bands (3060, 1000, 900 and 750 cm^{-1}) and the aliphatic bands (2920,1440 and 1320 cm^{-1}). **Figures 7 and 8** are the plots of the results for each of these regions. In both the C=O / C-O and the aromatic (**Figure 7**) regions there was no

detectable or only a very small change over the samples for either the 3eV or 6eV results. In the aliphatic region (**Figure 8**), there are clearly changes in the intensity over the 16AP -12AS - 2AP range; they will be discussed hereunder.

DISCUSSION

Original HREELS Spectra

Without computer treatment, the broad features of the low resolution original spectra (**Figure 2**) can still provide direct information about differences between the structural isomers. As indicated in the preceding section, the three regions - bands associated with aromatics, aliphatics and C=O / C-O- will be discussed separately.

Between the 3 and 6eV spectra, there is an apparent increase in intensity of the aliphatic associated bands ($2920, 1440, 1320 \text{ cm}^{-1}$) for the 16AP sample; this intensity increase induces an apparent resolution decrease in region 1- this behavior cannot be evidenced for the other two materials. It is expected that, if a resonance for the aliphatic chains takes place in the HREELS experiment, it would be observed at 6eV (**5**). As the surface region of the 16AP sample is supposed to contain the least aliphatic signal, our observation cannot now be rationalized; so this information will not be used.

Considering the CH stretch region ($2900 - 3000 \text{ cm}^{-1}$), it is very clear (especially on the 3 eV

spectra) that the aliphatic/aromatic intensity ratio grows from the 16AP to the 2AP materials: the 16AP C-H band is "aromatic-like" with an aliphatic shoulder at lower loss energy; the 2AP band is "aliphatic-like", with an aromatic shoulder at higher loss energy. This intensity variation should be related to the varying position of the aromatic rings along a constant aliphatic backbone.

Maximum Likelihood Spectral Restoration

The trends found in the original spectra carried through into the SSRES results (**Figure 3**). The relative intensities of the CH stretching bands indicated, now more clearly, the increase in the ratio between the aromatic and aliphatic CH stretches as the carboxyl anthracene group changed positions along the fatty acid chain.

There is slightly more intensity in the aliphatic region at 6eV spectra than at 3eV for the 16AP sample. The bands associated with the aromatics and C=O / C-O species are not enhanced either in the 3 to 6eV spectra. This may again indicate a resonance effect is contributing to the HREELS spectra of these isomers.

Curve Fitting

The FIT program was employed because - a priori - absolute intensity is not preserved in the restoration program. Once again it was shown that the FIT results were reproducible. The FIT

band positions, which were either held or allowed to shift without restriction also correlated with the band positions determined from SSRES within 30 cm^{-1} in most cases (**Figure 4**). The trends seen in both the original data and the restored spectra were again seen in the FIT results.

Peak Intensities vs Functional Group Location

The areas of each of the ten bands corresponding to functionalities within the three isomers were normalized to the elastic peak, to follow the effect of varying functional group position (**Figures 7, 8 and 9**). The functionalities of interest were considered into three groups: aromatic (3060 , 1000 , 900 and 750 cm^{-1}), aliphatic (2920 , 1440 and 1320 cm^{-1}) and carbonyl/ester (1725 , 1600 and 1170 cm^{-1}).

Aromatic. For both the 3 and 6 eV data, the plot (**Figure 7**) of all of the aromatic band intensities are straight lines with a slope near zero, within experimental error. The 2AP 6eV data point is considered artificially high due to the difficulty in SSRES and FIT to recognize these groups; moreover, as there was only one successful experimental spectrum, there is no strong evidence that there is a real increase in the aromatic intensity with 6eV impact energy. Except for the 1000 cm^{-1} band, the 6eV data is the same as the 3eV data, within experimental error. This indicates that there is **no resonance effect on the aromatic vibrational bands**, and no apparent sensitivity of sampling depth for vibrations due to the aromatic functionalities. The last point is contrary to what was expected, and what has been suggested from the examination of the original spectra and the SSRES results. This is because of the tendency to consider the intensities due to

aliphatic vibrations as constant; when in fact, as is shown below, this is not true. Because of the ratio technique either the aromatic vibrational intensities are decreasing **or the aliphatic vibrational intensities are increasing**. It is shown below that the latter is occurring. Thus, the depth from which aromatic signals can be detected is at least 20 .

Carbonyl/Ester Similar to the aromatic band results, the plot (**Figure 8**) of the carbonyl associated bands are straight flat lines within experimental error, with a very slight difference for the 6eV data points which were higher than the 3eV ones; this is probably too small to indicate a resonance effect contribution at 6 eV in the carbonyl/ester vibrations.

Aliphatic The plot of the aliphatic band intensities (**Figure 9**) shows a definite increase in intensity from the 16AP to the 2AP structures. The intensities of the 6eV data points are also slightly higher than the 3eV experiment, indicating the aliphatic vibrations are resonance enhanced around 6 eV impact energy. The overall trend at both impact energies clearly suggests that there is sampling depth sensitivity in the aliphatic vibrations, with more aliphatic CH bends and stretches detected in the 2AP film than the 16AP film. This follows from the isomer structures, where more of the aliphatic tail is near the surface in the 2AP isomer than in the 16AP isomer. In the 16AP isomer, signal from the aliphatic tail would be attenuated by the carboxyl and anthracene functionalities.

CONCLUSIONS

The results from previous work indicated that HREELS had a shallow sampling depth in organic films, ranging from 3 - 20 Å (2-5). In this work, three Langmuir - Blodgett films of structural isomers were analyzed to precisely determine the effective sampling depth by using films with distinct functional groups at three different positions along a similar long chain aliphatic tail. Each spectrum was analyzed into contributions to three regions: bands due to aliphatic, aromatic and carbonyl/ester vibrations. The latter two fingerprint chemical groups at different positions along a constant aliphatic tail in a- supposedly- well ordered monolayer film.

Effectively, the correct intensity trend is seen on the original spectra and on the SSRES restored ones; but our attempts to derive exact information depths using quantitative information from the curve fitted data (FIT) have not been conclusive.

The **aromatic bands** (C-H stretch at 3000 cm⁻¹) were excited through the depth of the film (on the order of 20 Å). The aromatics were detectable at all depths, only with a decreasing relative intensity from 16AP to 2AP. The **aliphatic groups** were detectable at all positions relative to the carboxyl anthracene location, with intensity variations suggesting a resonance mechanism was involved.

Enhancement of CH modes had previously been noted by Wandass (5) in Langmuir-Blodgett films of fatty acids. Apai and McKenna observed enhancement of aromatic and aliphatic CH

modes at or above 5eV, as well as of carbonate modes for impact energies of 3.5 eV in a polycarbonate film (7).

The results of this study show that different functional groups (aliphatic carbons, aromatic ones, C=O groups...) within an organic film may have a *different depth sensitivity*, especially if resonance effects are present. The intensity of bands due to aliphatic functionality was increased for the 12AS and 2AP samples. In these samples, relatively more aliphatic structure is placed closer to the surface, as the aromatic sidechain is further away from the surface. The intensity of the aliphatic bands dominates the spectrum and overwhelms the signal from aromatic and carbonyl vibrations. In previous studies methyl and methylene groups showed greatest intensity in a fatty acid film (2,4,5) or polyethylene film (3) indicating a larger surface sensitivity for these vibrational bands.

Further studies with longer series of structural isomers are planned to add data to a sampling depth curve for organic films studied by HREELS. These studies should use different primary impact energies and scattering geometries to make the sampling mechanisms more clear.

ACKNOWLEDGEMENTS

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Table I
Vibrational Bands of Interest

Region	Band Position (cm⁻¹)	Assignment	Intensity¹	
			Infrared	Raman
1	3060	Aromatic CH stretch	m	s
1	2920-2800	Aliphatic CH stretch	vs	s
2	1725	Carbonyl stretch	vs	m
2	1600-1560	Carbonyl stretch and ring breathing	w	s
3	1440-1410	Aliphatic CH bend	m	vs
3	1360	Aliphatic CH bend	m	m
3	1280-1260	Aromatic	s	s
3	1190-1180	Ester bend	vs	m
4	1000	CH out-of-plane deformation	m	s
4	900	CH out-of-plane deformation	m	w
4	780-750	CH out-of-plane deformation	s	s

1. key to Intensity: vs = very strong, s = strong, m = medium, w = weak,

Figure captions

Figure 1 Structures of Model Film Molecules 16AP: 16-(9-anthroyloxy) palmitic acid , 12AS: 12-(9-anthroyloxy) stearic acid, 2AP: 2-(9-anthroyloxy) palmitic acid

Figure 2 HREELS Spectral Data

- | | |
|------------------------------|------------------------------|
| a. 16AP at 3eV Impact Energy | b. 16AP at 6eV Impact Energy |
| c. 12AS at 3eV Impact Energy | d. 12AS at 6eV Impact Energy |
| e. 2AP at 3eV Impact Energy | f. 2AP at 6eV Impact Energy |

Figure 3 HREELS Spectral Data and Restoration Results at 3 eV

- | | |
|------------------------------|---------------------|
| a. 16AP HREELS Spectral Data | b. 16AP Restoration |
| c. 12AS HREELS Spectral Data | d. 12AS Restoration |
| e. 2AP HREELS Spectral Data | f. 2AP Restoration |

Figure 4 Comparison of Results from 16 AP

- a. 3eV Restoration b. FTIR Spectrum c. FT-Raman Spectrum

Figure 5 FIT Results for 16AP, 3eV Impact Energy

Top: 3450 - 2480 cm^{-1} Bottom: 2000 - -250 cm^{-1}

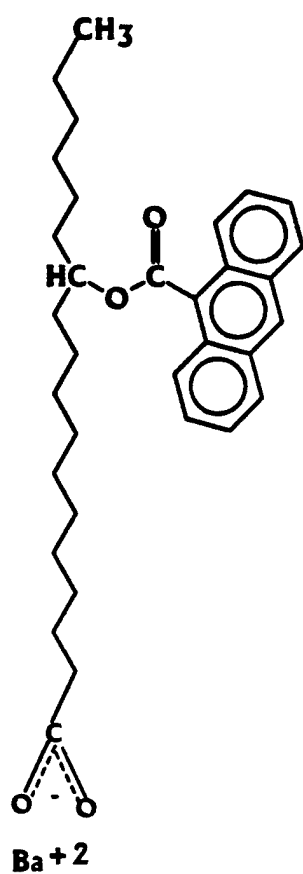
Figure 6 FIT Results for 2AP, 3eV Impact Energy

Top: 3450 - 2480 cm^{-1} Bottom: 2000 - -250 cm^{-1}

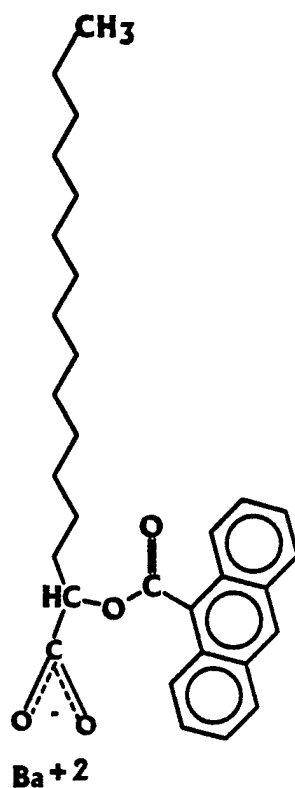
Figure 7 Plot of the ratio of "aromatic" Band Area to Elastic Peak Area vs Apparent Depth of the Anthroyl Structure
Data taken at 6 eV are offset by 2 Å to the right

Figure 8 Plot of the ratio of "carbonyl-ester " Band Area / Elastic Peak Area vs Apparent Depth of the Anthroyl Structure
Data taken at 6 eV are offset by 2 Å to the right

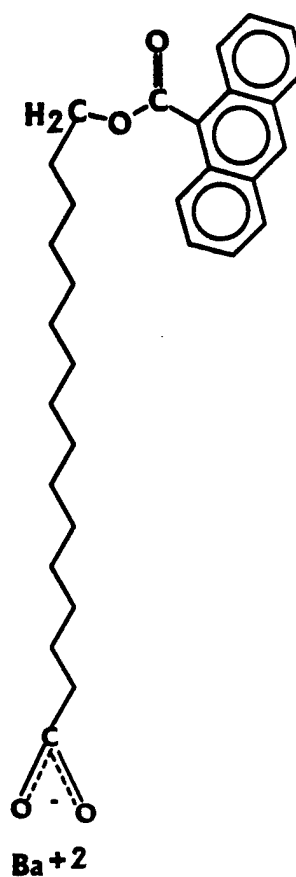
Figure 9 Plot of the ratio of "aliphatic" Band Area / Elastic Peak Area vs Apparent Depth of the Anthroyl Structure
Data taken at 6 eV are offset by 2 Å to the right



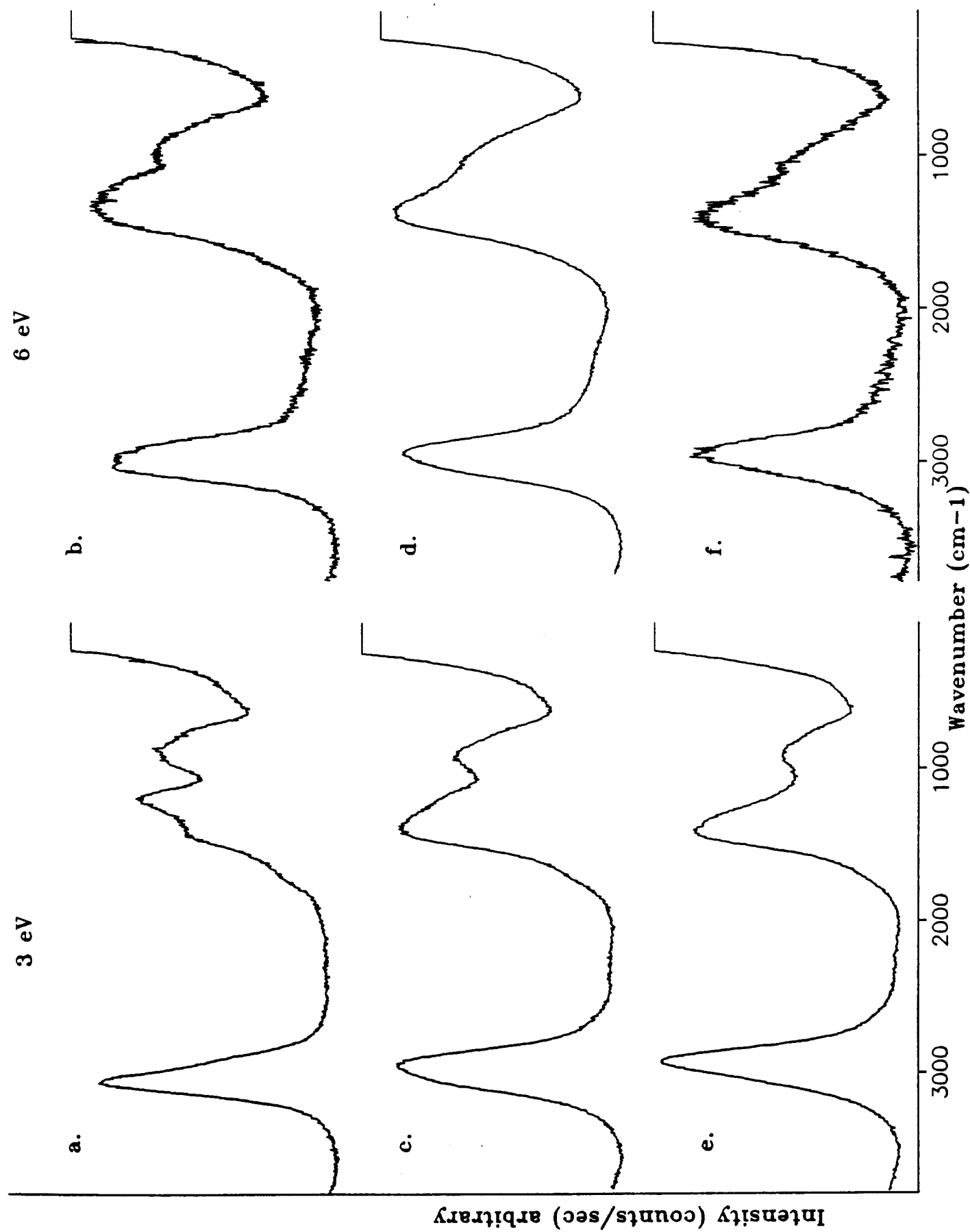
12 AS



2 AP

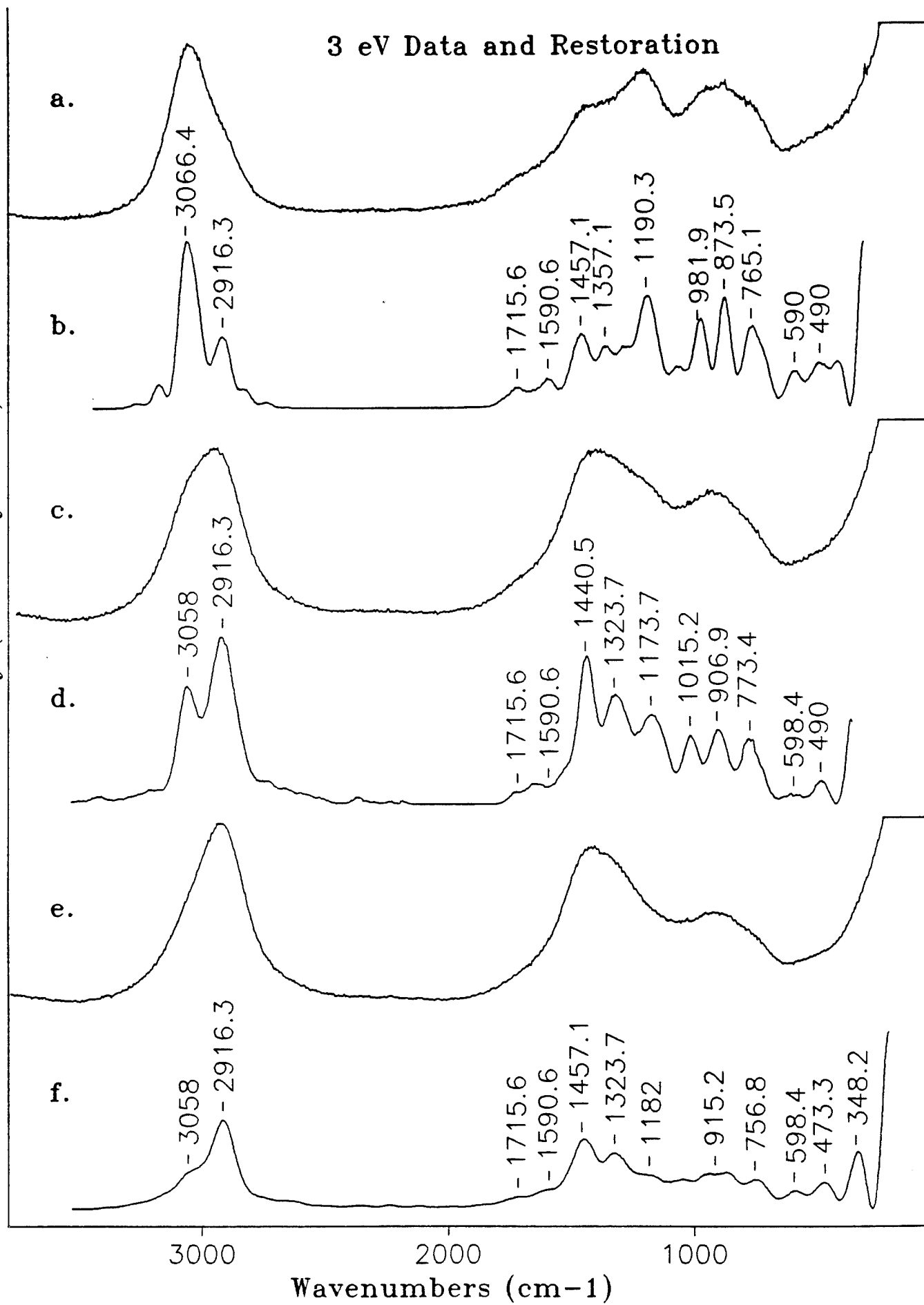


16 AP

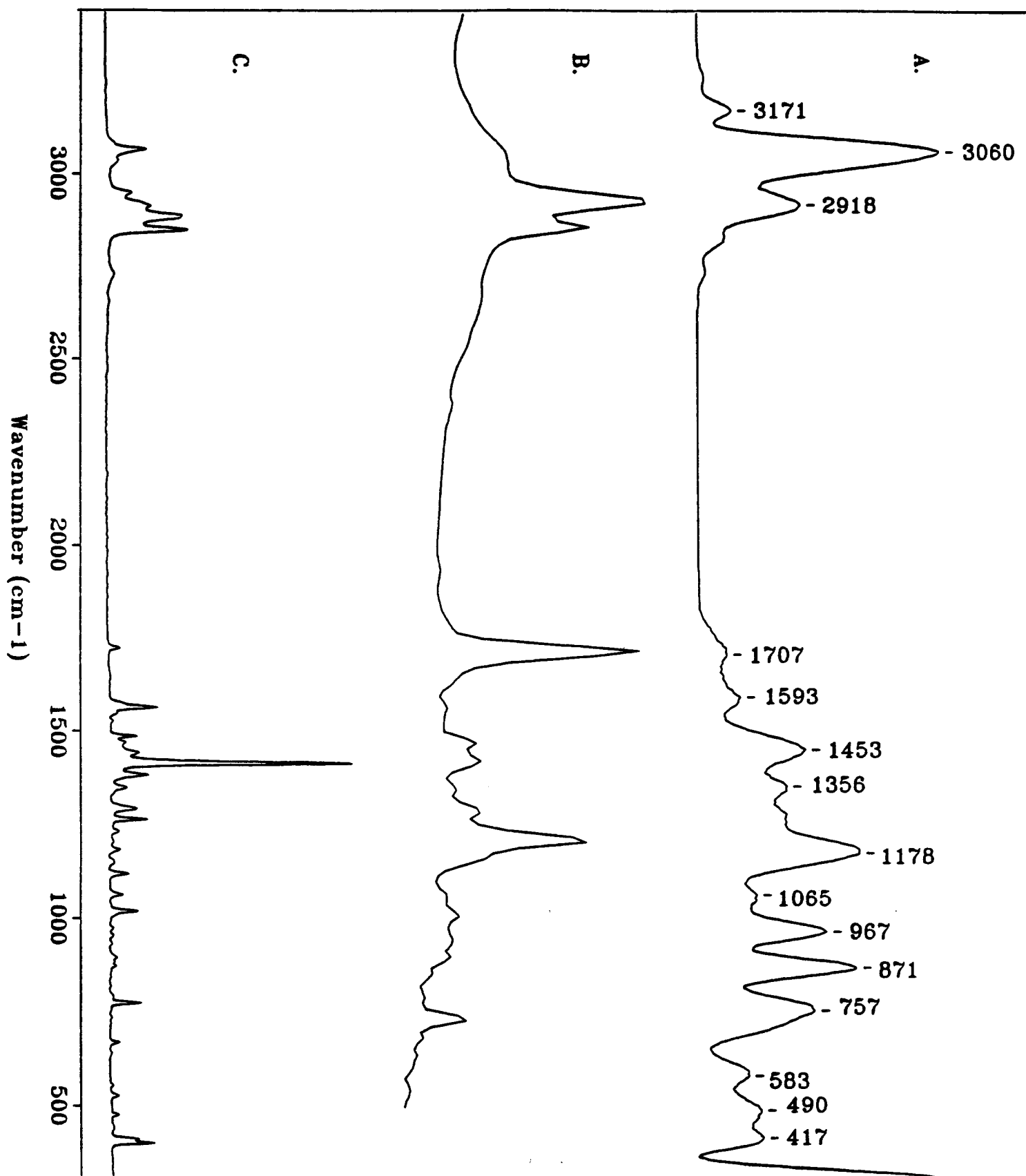


3 eV Data and Restoration

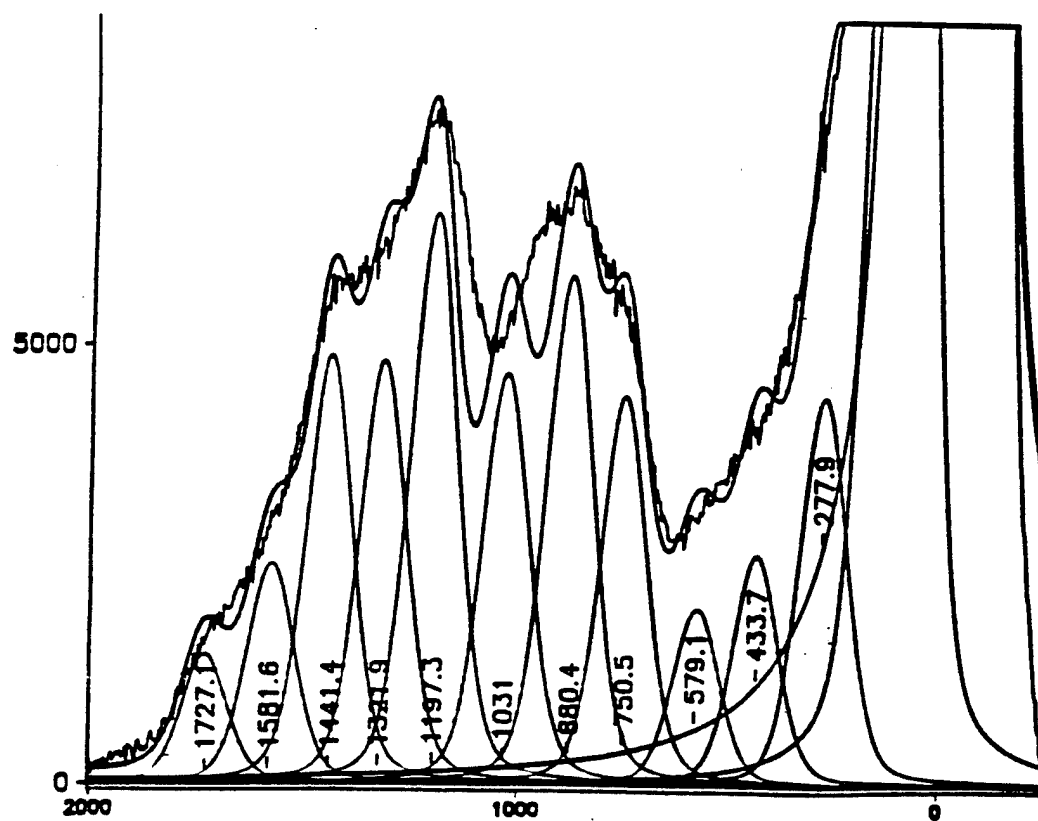
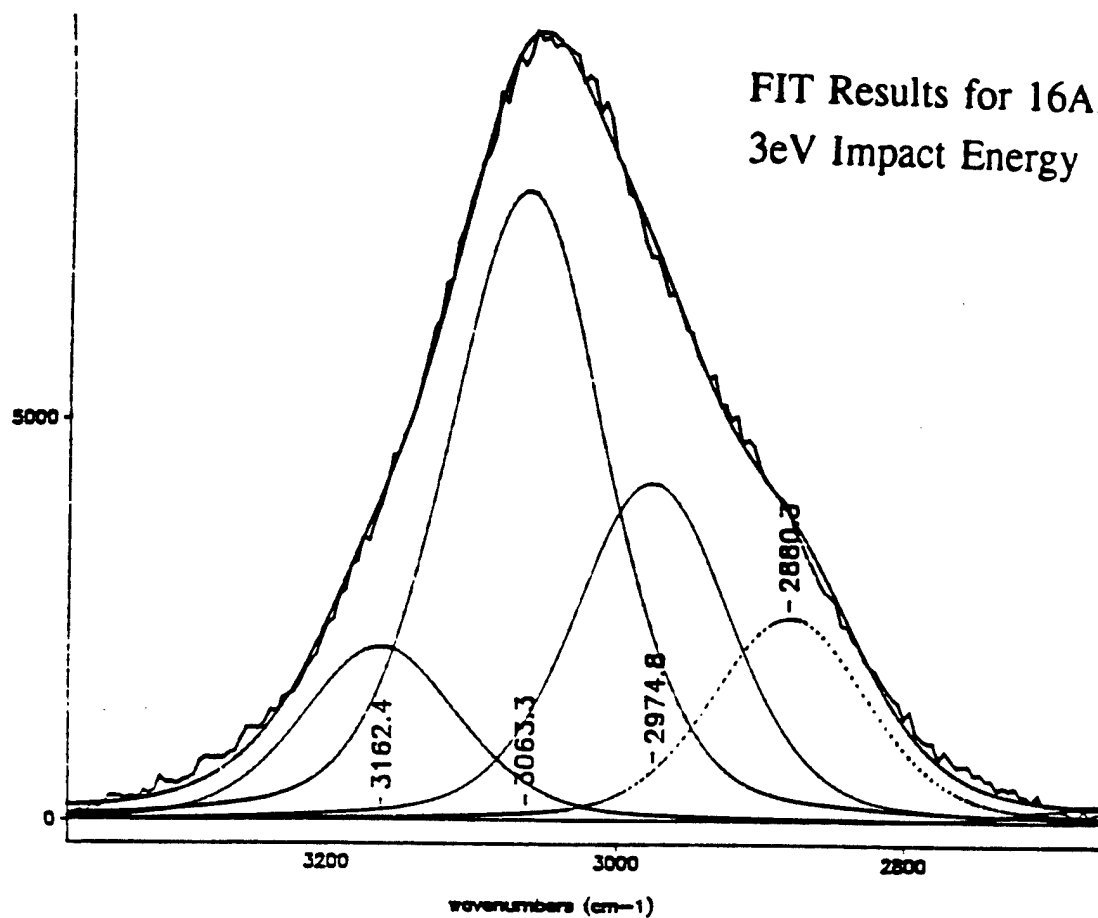
Intensity (arbitrary units)

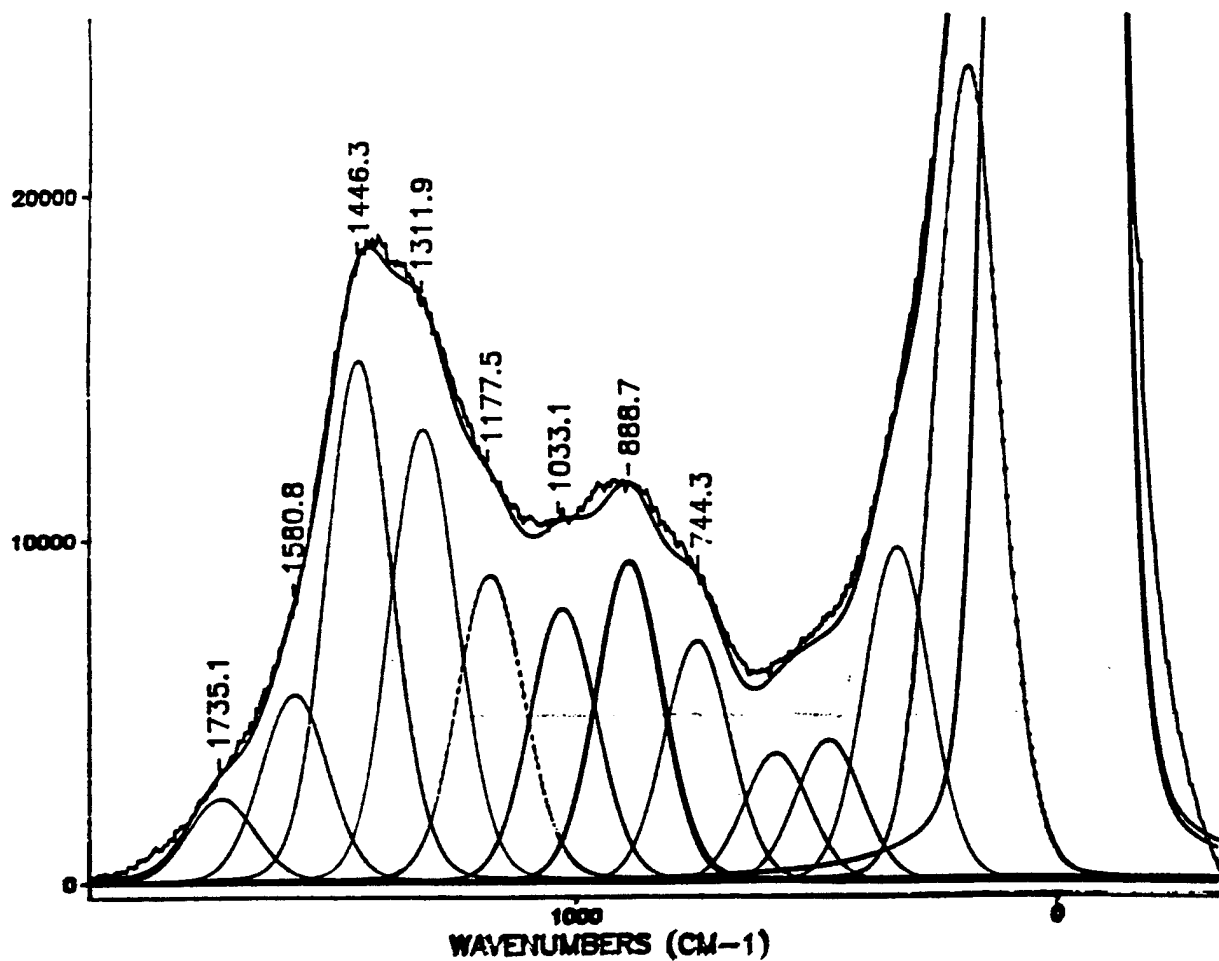
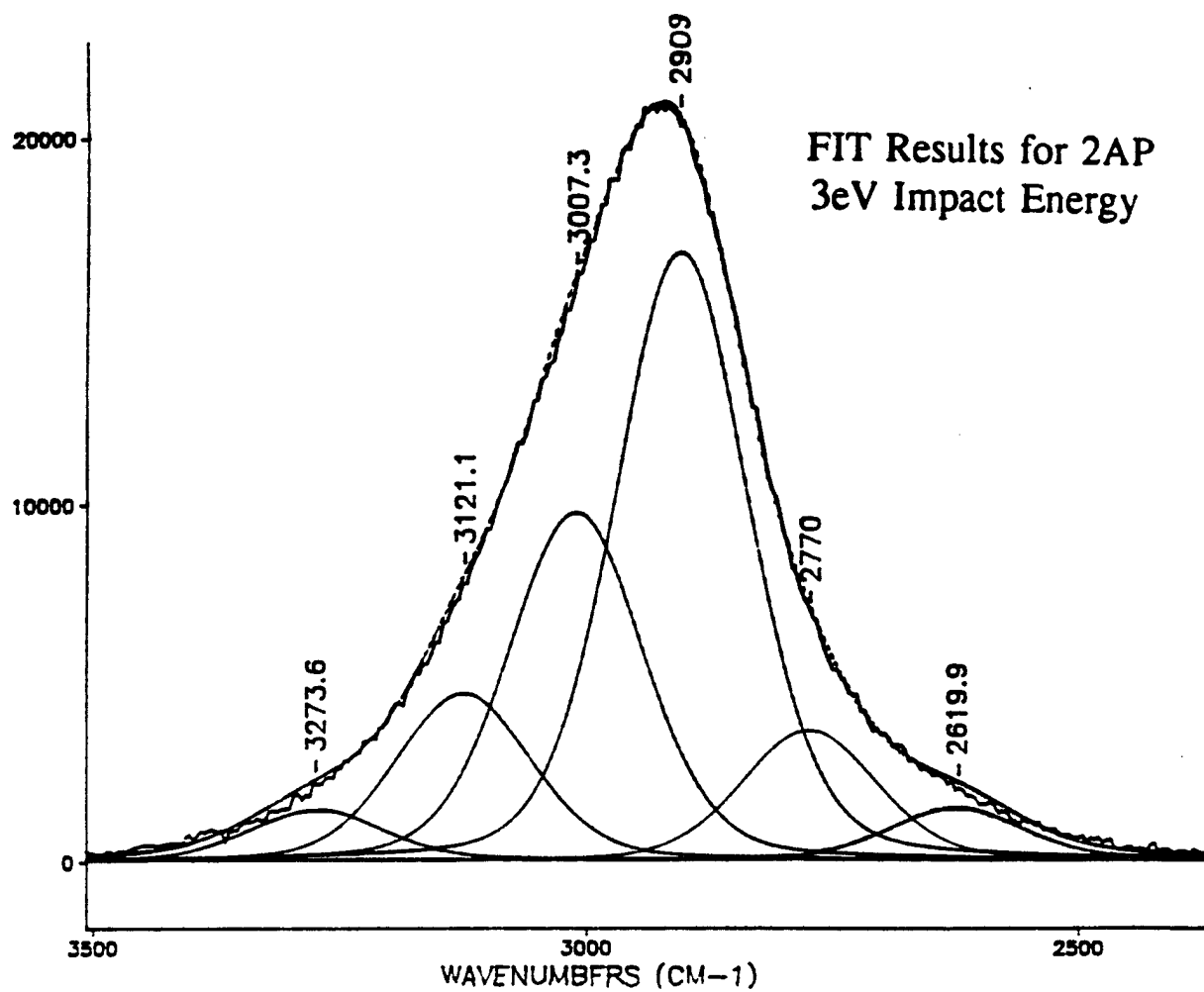


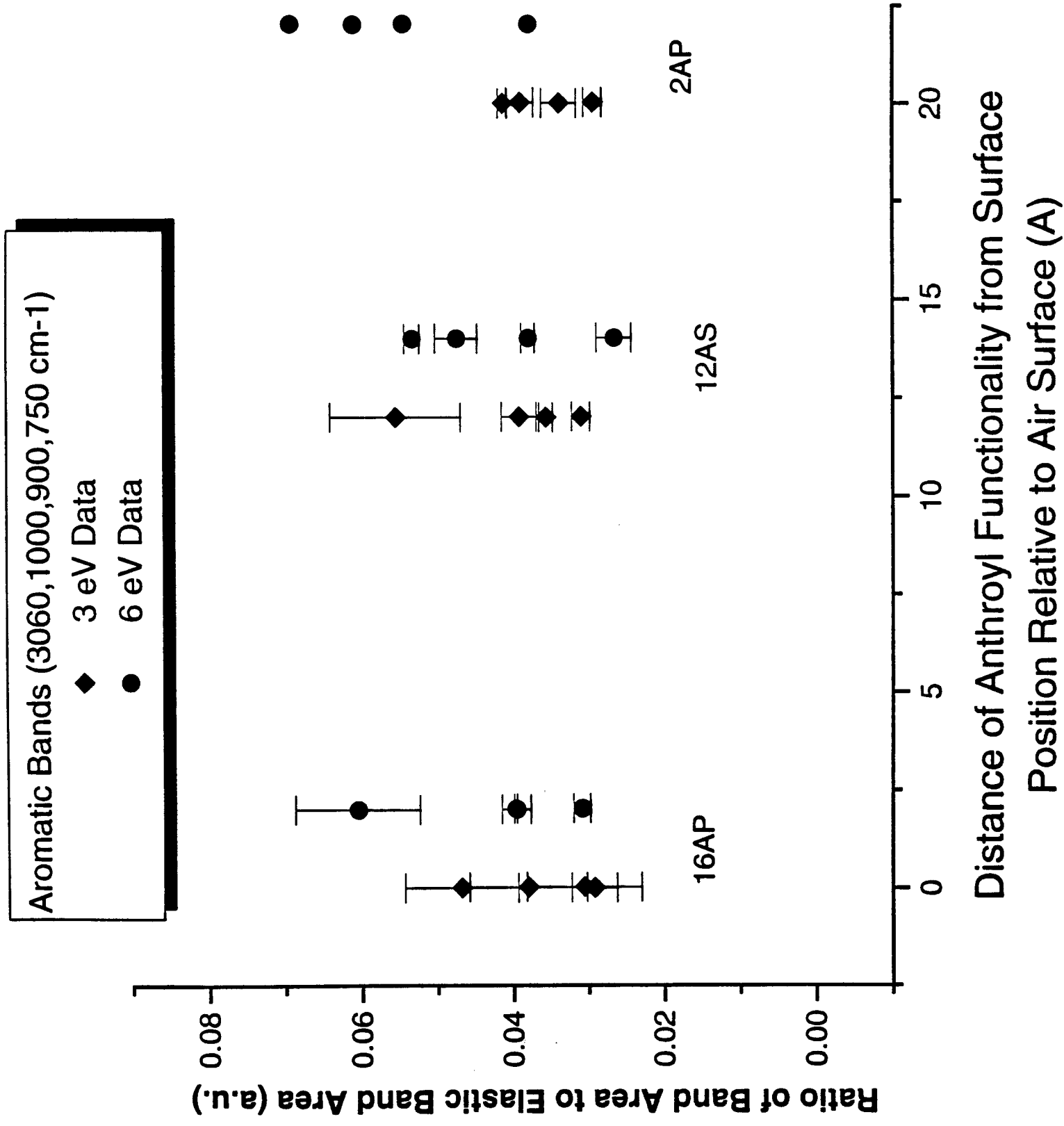
Relative Intensity (a.u.)

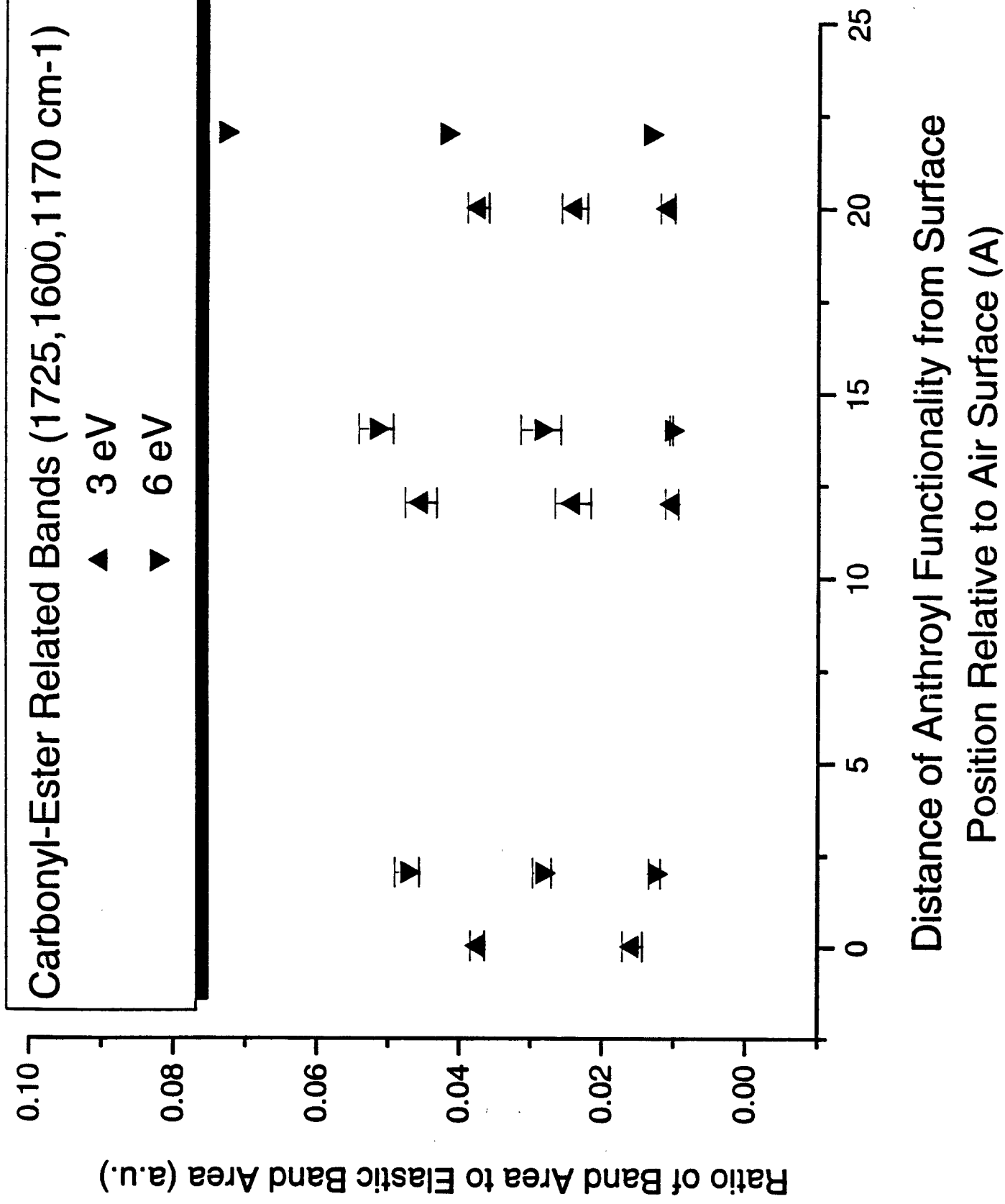


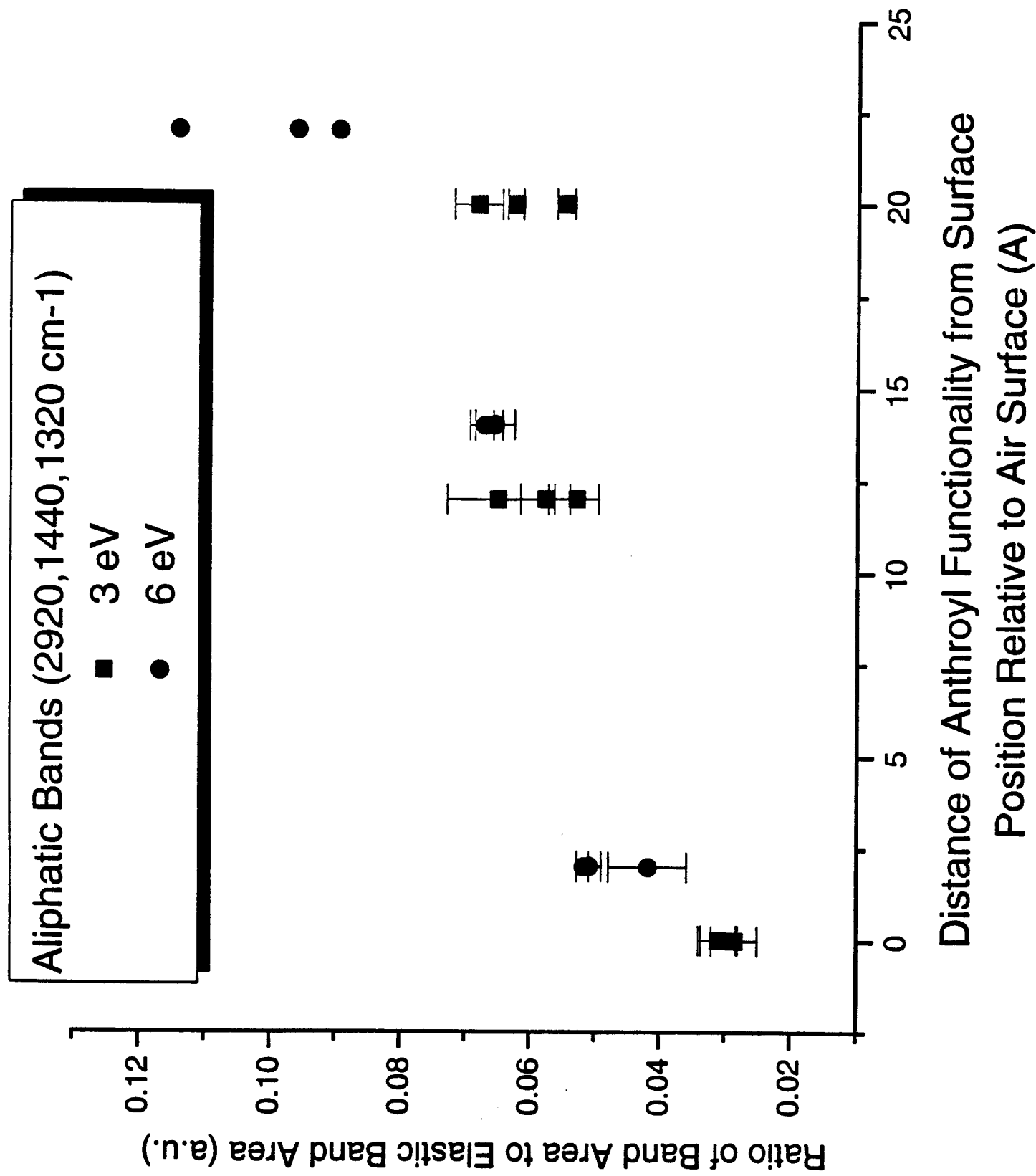
FIT Results for 16AP 3eV Impact Energy











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